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INT CL[6] B05B 1/02 1/22, B05C 5/02, B05D 1/26 1/30
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(54) Abstract Title
Selective deposition of organic films

(57) To provide a patterned film particularly in the field of integrated electronic and optoelectronic devices, a solution-processible organic material is selectively deposited by supplying said material through an elongate hollow bore 10 from a remote end in communication with a reservoir 14 of said material to a distal end adjacent a substrate 2 for receiving said material, wherein the supply of said material is controlled such that by virtue of contact between said material and the substrate it leaves the distal end under one or a combination of gravitational force and wetting tension. The material may be deposited on to electrode material 4 which has been predeposited in regions defined by separating material 6.

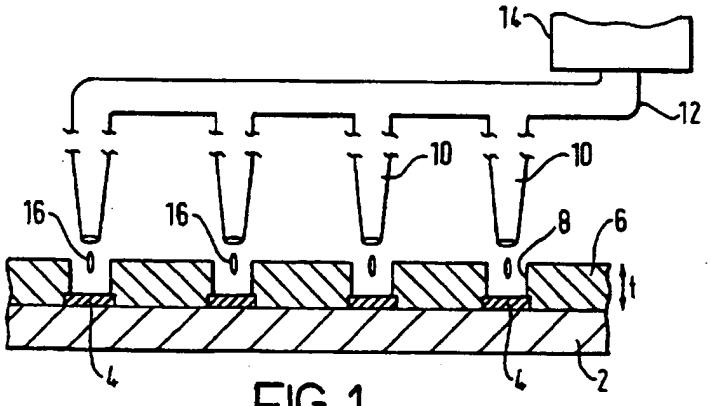

FIG. 1

GB 2 336 553 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

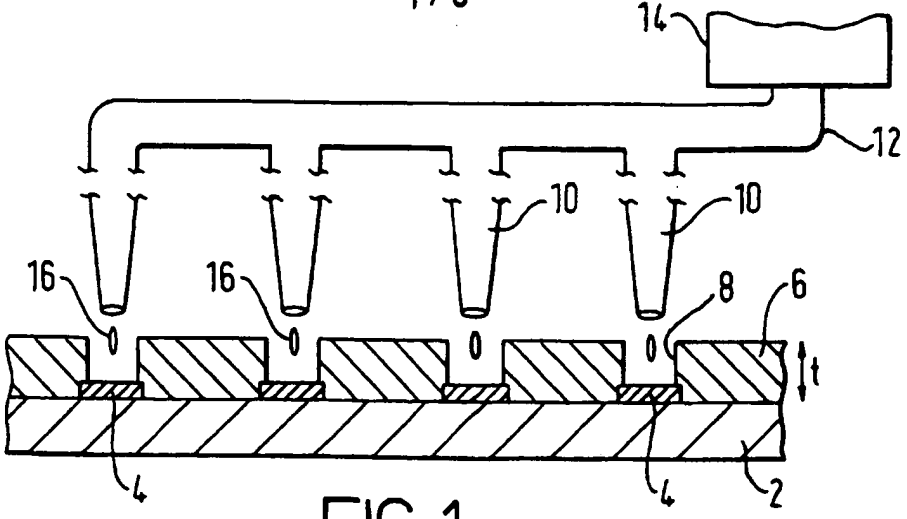

FIG. 1

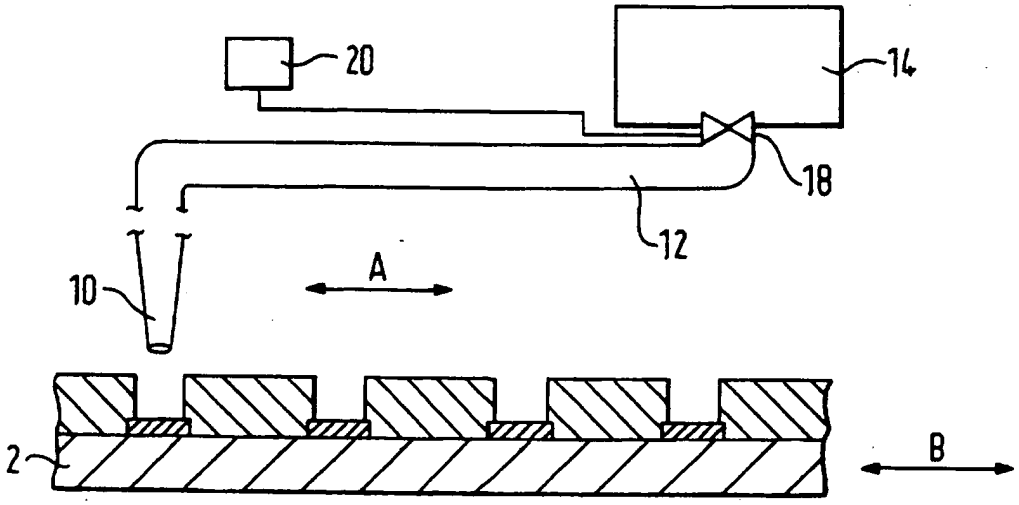

FIG. 2

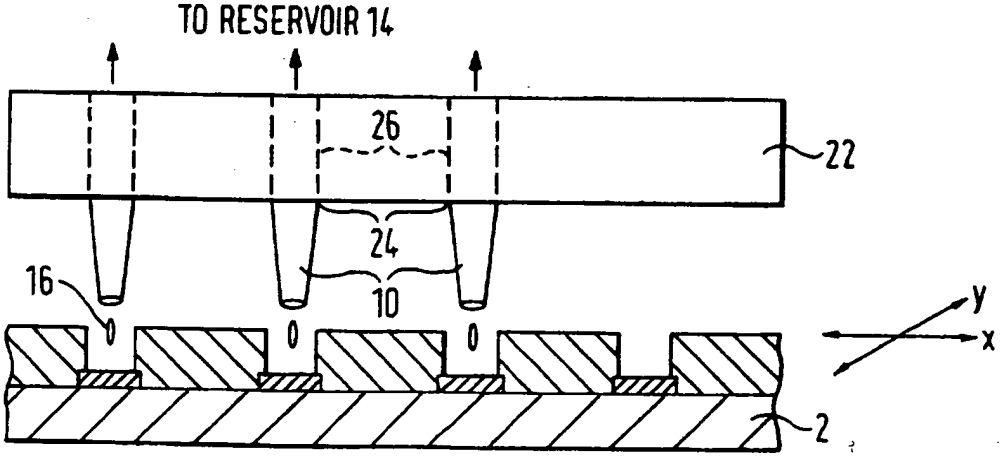

FIG. 3

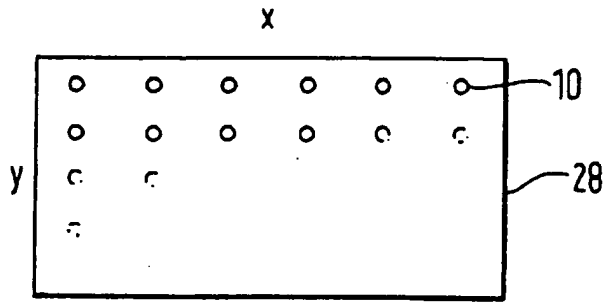

FIG. 4

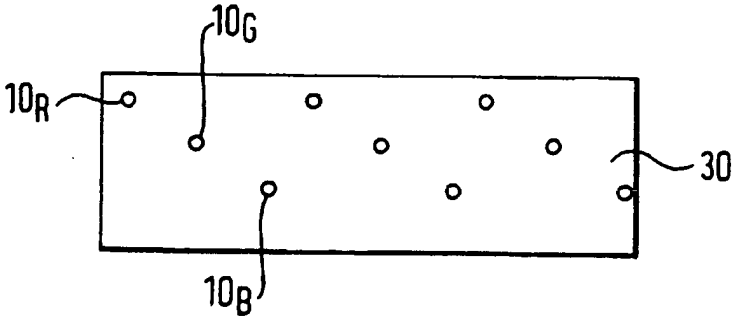

FIG. 5a

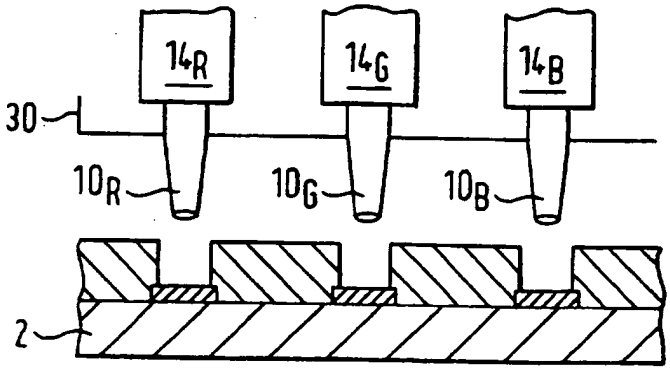

FIG. 5b

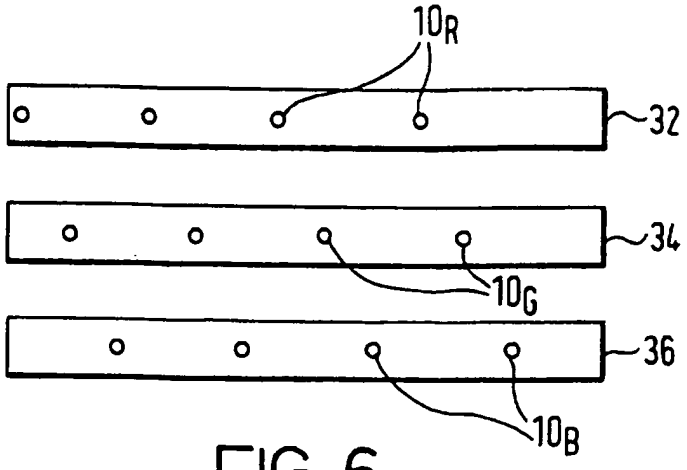

FIG. 6

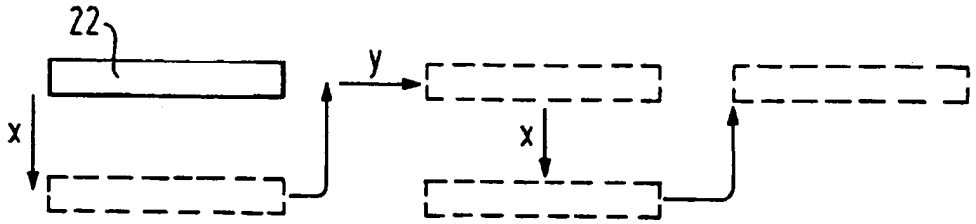

FIG. 7

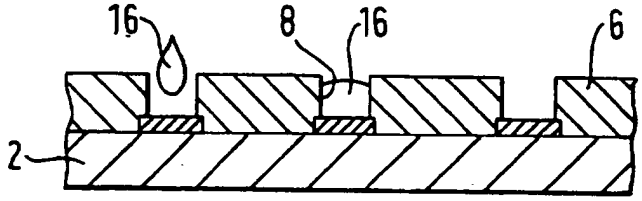

FIG. 8a

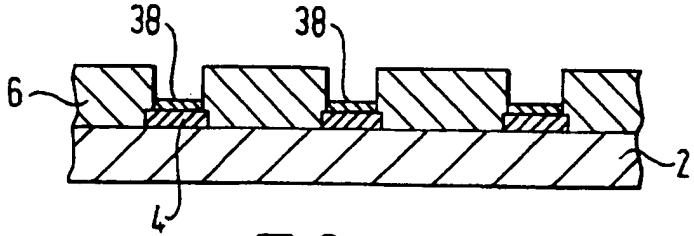

FIG. 8b

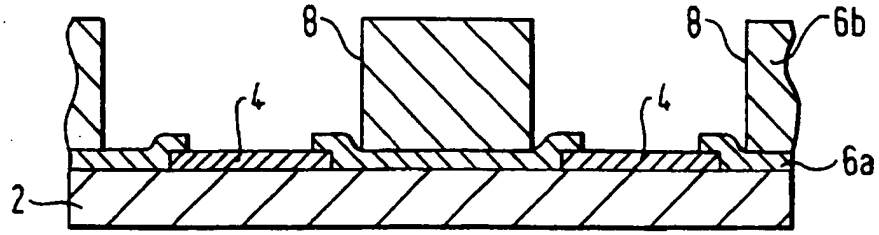

FIG.9a

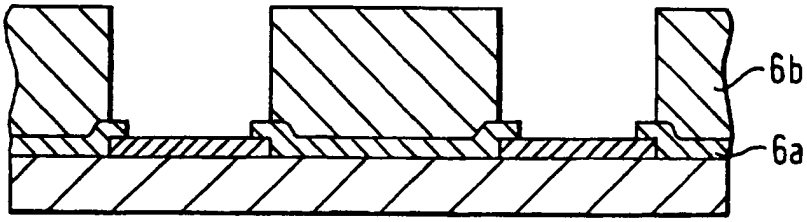

FIG.9b

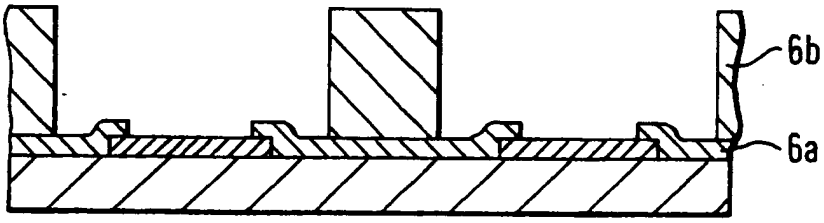

FIG.9c

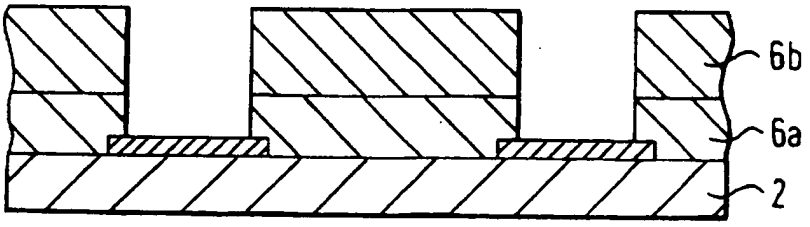

FIG.9d

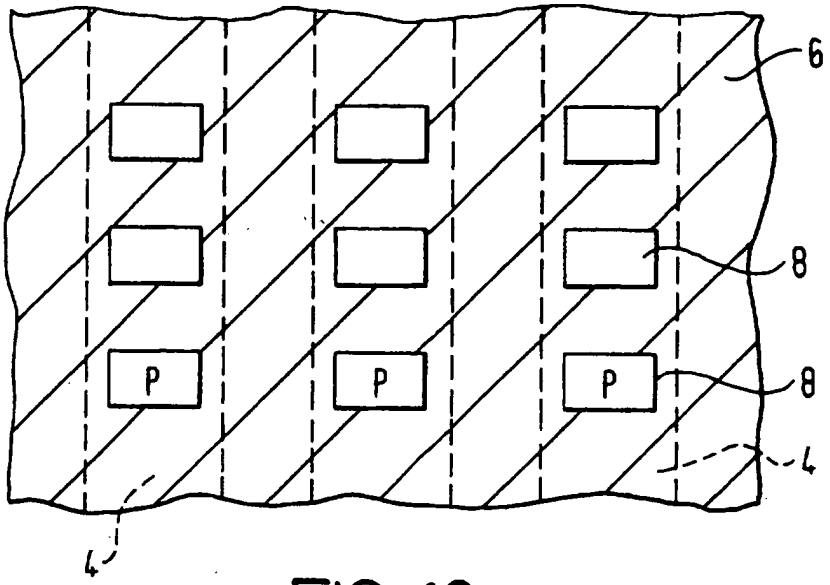

FIG. 10

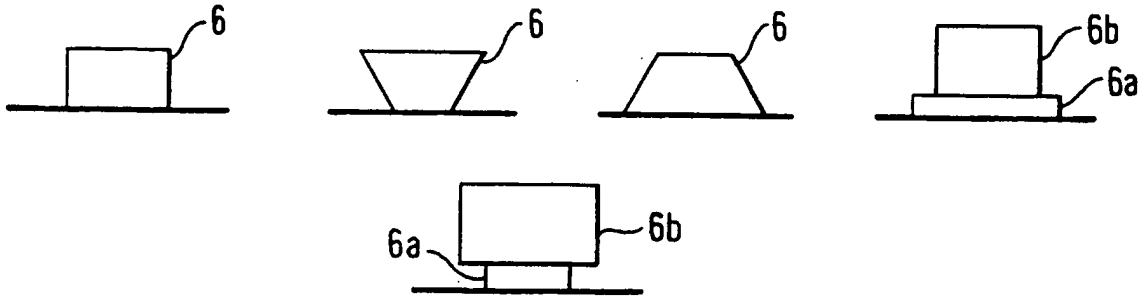

FIG. 11

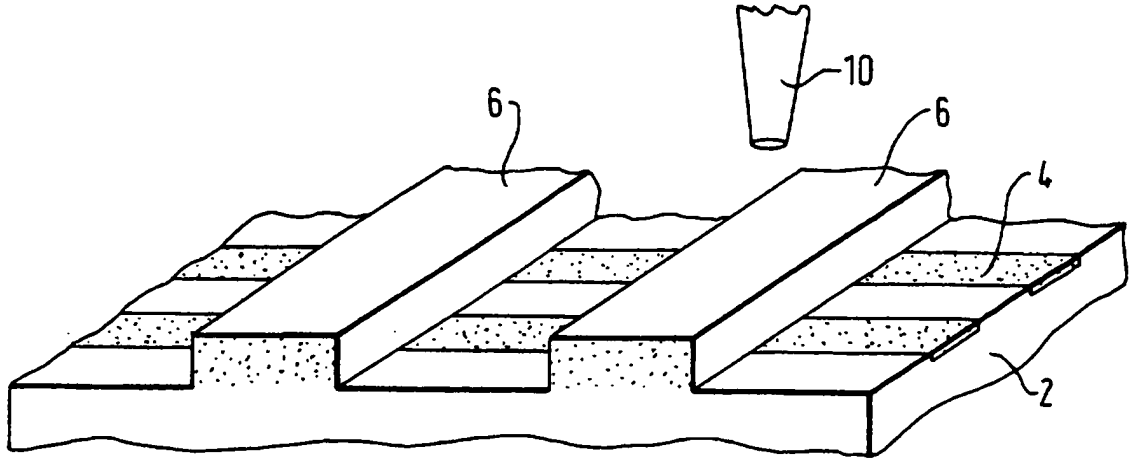

FIG. 12

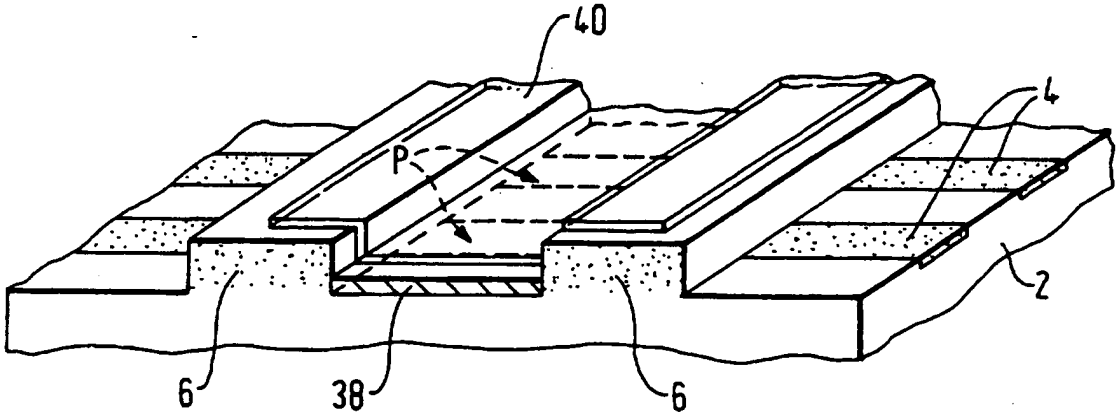

FIG. 13

SELECTIVE DEPOSITION OF POLYMER FILMS

This invention relates to a method of selectively depositing solution-processible films so as to provide a patterned film particularly in the field of integrated electronic and optoelectronic devices.

Many integrated electronic devices require patterning of one or more thin layers which are employed in these devices at various levels of resolution. This is the case for organic electronic and opto-electronic devices, that is devices which include at least one electrically active or opto-electrically active organic layer. Such devices include patterned and/or multi-colour organic light-emitting devices (OLEDs) and particularly those incorporating light-emitting polymers (LEPs). Such organic layers can be organic conductors such as conductive polymers (polyaniline, polyethylenedioxythiophene and other polythiophenes, polypyrrole, etc and their doped forms) or fluorescent organic compounds and conjugated polymers such as Alq3, polyphenylenes and derivatives, polyfluorenes and derivatives, polythiophenes and derivatives, polyphenylene vinylenes and derivatives, polymers containing hetero-aromatic rings, etc or generally conjugated compounds (molecules and polymers) capable of sustaining charge carrier transport, or organic semiconductors.

OLEDs such as described in US Patent No. 5,247,190 or in US Patent No. 4,539,507, the contents of which are incorporated herein by reference are flat-panel displays which incorporate electronically active thin organic layers such as mentioned above. In US 5,247,190 the active organic layer is a light-emissive semiconductive conjugated polymer and in US 4,539,507 the active organic layer is a light-emissive sublimed molecular film. These displays include first and second electrodes capable of injecting charge carriers of opposing types into a light-emissive layer. When an electric field is applied between the electrodes, charge carriers of opposing types are injected into

the light-emissive layer, where they recombine and then decay radiatively to emit light. The wavelength of the emitted light can be adjusted by selecting the light emitter polymer layer appropriately to thereby alter the colour which is emitted. Other layers can be included, for example it is possible to include a charge transport layer between one or both of the electrodes and the light-emissive layer to assist in charge carrier injection from the electrodes to the light-emissive layer. Alternatively, more than one light-emissive layer can be included to provide another way for controlling the colour of emitted radiation. Such displays are described in detail in the preceding referenced US patents and thus are not described in further detail herein.

Other organic optic, electronic and opto-electronic devices are patterned colour filters for LCD displays, patterned fluorescent films, photo-diodes and photo-voltaic cells, thin-film transistors, diodes, triodes, opto-couplers, image intensifiers, etc and various combinations of such devices in integrated electronic circuits.

High performance of optic, electronic and opto-electronic devices incorporating such active organic layers requires great care in the deposition and processing of the organic layers. When "compromises" are made in the processing and deposition of these layers the device performance often deteriorates. Such "compromises" however are often required, for example to fabricate devices in which one or more of the active organic layers need to be patterned, for example to make a multi-colour red-green-blue (RGB) LEP device.

Various patterning techniques have been investigated and developed to fabricate patterned organic thin-film devices, most of which are very limited in their applicability and/or have disadvantages in the sense of having device performances poorer than the unpatterned equivalent devices. These patterning techniques include evaporation through shadow masks or at

specific angles and using separators on the device substrates, both of which are used for patterned devices using sublimed organic films. However, these techniques have size and/or resolution limitations and are not really applicable for solution-processed materials such as conjugated polymers. Various photo-lithographic patterning techniques can, in principle, be used to pattern organic thin films but this often results in a contamination of interfaces and a degradation of device performance. In many cases the techniques (UV light, baking steps, etc) and chemicals (photo-resists, etch and developer solutions, solvents, etc) used during lithographic processing are only just compatible with active organic layers, if at all. All these techniques also add additional processing steps and hence cost.

As an alternative for depositing materials which can be solution processed, ink-jet printing has been under investigation to fabricate devices with high-resolution patterns. Although ink-jet printing is a very attractive technique to fabricate patterned devices because it directly "writes" the patterns on the substrate without the requirement for additional subsequent patterning steps, it also puts constraints on the processing: the ink-jet printed solutions containing the active organic material(s) need to fulfill a range of requirements related to solution viscosity, concentration and/or wetting properties with the ink-jet print-head. Also, this technique is investigated to pattern high-resolution devices with the appropriate high-resolution print-heads and hence ink-jet drop-sizes tend to be small which has implications on throughput. Therefore, if larger displays (or other devices) need to be fabricated with larger pixels or "spaced areas", for example in excess of 50 μm or even in excess of several 100 μm, but for which the resolution requirements may not be very high, the attractions of high-resolution ink-jet printing decrease.

It is an aim of the present invention to provide a patterning and deposition technique for solution-processible materials used as

active thin films in optic, electronic and opto-electronic devices, which mitigates or eliminates the above disadvantages.

According to one aspect of the present invention there is provided a method of selectively depositing a solution-processible material by supplying said material through an elongate hollow bore from a remote end in communication with a reservoir of said material to a distal end adjacent a substrate for receiving said material, wherein the supply of said material is controlled such that it leaves the distal end under one or a combination of gravitational force and wetting tension by virtue of contact between said material and the substrate.

The wetting tension comes into play as a droplet of material is brought into contact with the substrate while it is still "attached" to the distal end of the bore. It causes the substrate to "pull" the droplet from the distal end of the bore. The wetting tension is controllable through the surface tension qualities of the material in association with the configuration of the droplet as it leaves the distal end of the bore, the wetting angle of the droplet with the substrate, capillary forces from the bore and pressure from the reservoir. The use of wetting tension allows a more controllable and static deposition process. However, for depositing large areas it is also possible that the predominant force is gravitational, that is that the droplet leaves the distal end of the bore prior to making contact with the substrate.

The transfer speed and amount of material supplied through the elongate hollow bore is preferably controlled by selecting a combination of parameters including the cross-sectional area of the bore, the distance from the substrate and the time and pressure applied at the reservoir.

According to another aspect of the present invention there is provided a method of manufacturing an optic, electronic or optoelectronic device comprising:

(a) forming on said substrate a predetermined configuration of separating material to define predetermined regions for subsequent deposition of a solution-processible material;

(b) depositing a solution-processible material in said predetermined regions by supplying said material from a remote end of an elongate hollow bore in communication with a reservoir of said material to a distal end of said bore adjacent said predetermined regions,

wherein the supply of said material is controlled such that it leaves the distal end under one or a combination of gravitational force and wetting tension by virtue of contact between said material and the substrate; and

(c) performing a drying step.

In one arrangement, said at least one hollow bore is in communication with said reservoir via a flexible tube to allow movement of said bore relative to said substrate to permit selected deposition at predetermined regions of the substrate. In another arrangement, the elongate hollow bore forms part of a bore assembly which includes the reservoir and which is movable relative to the substrate. In a still further arrangement, the substrate is mounted for movement with respect to said at least one elongate hollow bore.

The bore assembly can comprise an array in the form of a plate comprising a plurality of apertures each of which is associated with a respective protruding elongate hollow bore, said apertures permitting communication of said bores with said reservoir.

To provide different materials, e.g. different colours, more than one hollow bore can be provided.

To provide a multicolour light emitting device, there can be three such elongate hollow bores in communication with respective different reservoirs for supplying different material to predetermined regions of the substrate, said different materials being light-emissive organic materials capable of emitting light

at different wavelengths.

The substrate can carry a preformed configuration of separating material (so-called "bank") for defining predetermined regions where said selective deposition is to take place. To manufacture an optic, optoelectronic or electronic device, an electrode material can be predeposited in said predetermined regions prior to said selective deposition.

The control of droplet emission from the hollow bores can be controlled utilizing a number of factors, in particular the following:

i) cross-sectional area of the bore, preferably in the range 0.001 mm^2 to 10 mm^2 and/or preferably circular with a diameter greater than 50 microns and preferably greater than 200 microns;

ii) the distance between the substrate and the distal end of the elongate hollow bore, preferably less than 10 mm, preferably still less than 5 mm and still better less than 1 mm;

iii) the transfer speed of the material via said bore, preferably less than 3 m/s and preferably still less than 1 m/s;

iv) pixel spread areas which may be of any convenient shape, e.g. square, rectangular or circular and which preferably have a largest dimension greater than 50 microns and possibly greater than 100 microns, but preferably smaller than 3 mm and preferably still smaller than 1 mm. The preferred range of spread areas for which the invention is particularly useful is 250 μm^2 to 9 mm^2.

The method is particularly applicable for making a light-emitting

device in which said plurality of electrode regions are anode regions, and in which the method comprises a further step, after the drying step, of depositing a cathode layer. The solution-processible material in this context would be a light-emissive organic material, such as a suitable polymer.

Thus, the present invention relates generally to the patterning of solution-processible materials in optic/electronic/opto-electronic devices, particularly but not exclusively for LEP materials, using a novel deposition technique which is particularly amenable to the fabrication of patterned devices having large "spread areas", for example in excess of 50 microns and particularly in excess of 100 microns. The method allows for high throughput and low cost manufacture. In the preferred embodiment, the deposition technique is used in conjunction with substrates which include a bank of separating regions which define between them troughs into which processible material is dropped from one or an array of pipettes. The dropping of the solution-processible material can be controlled manually or automatically.

The deposition of the solution-processible material, in particular organics, e.g. polymers, from pipettes is a slower and more static process than ink-jet printing and thus issues which are normally pertinent with ink-jet printing such as polymer viscosity, surface tension and wetting angles are much less critical or irrelevant. With ink-jet printing, it is often necessary to add wetting agents and/or viscosity modifiers to the ink solutions to allow them to be deposited by the ink-jet technique. With the present invention, there is much less reliance on a need to modify the material itself.

The technique is described herein to define active pixel areas within an organic light-emitting device, but it will be appreciated that other applications are possible.

It is expected that the solution-processible material will emerge

from the pipette at a speed less than 3 m/s and preferably less than 1 m/s. The pipettes are preferably arranged vertically above the substrate, although they could be arranged at an angle. In the desired arrangement, the substrate is arranged at a distance from the distal end of the pipette which is sufficiently small that the drop which is about to be released from the distal end of the pipette is in contact with the "spread area" on the substrate before it leaves the pipette, so that wetting tension plays a part in creating a force to "pull" the droplet onto the substrate.

The volume released from the pipettes can be adjusted easily through dimensions of the pipette and time and pressure applied to the reservoir. Use can be made of existing automated precise micro-pipetting assemblies which currently have application in bio/pharmaceutical sciences, appropriately modified. Control over the deposition process can be obtained through the concentration of the solution-processible material, the amount of solution delivered, the wetting of the substrate over the active pixel areas and the bank separating material. In principle, the technique is much cheaper than ink-jet printing and allows for the possibility of a much higher throughput. Although the resolution of the active pixel areas defined by the present technique may not be as fine as is possible with ink-jet printing, nevertheless the advantages outweigh the disadvantages for devices with larger "spread areas".

Other preferred but not essential features distinguish the techniques described herein from ink-jet printing. The drop size utilised herein is larger than in a typical ink-jet process, and in the described embodiment the cross-sectional area of the bore is in the range 0.001 mm^2 to 10 mm^2.

In the deposition technique described herein, droplets are not ejected as in ink-jet printing but issue from the pipettes predominantly under the influence of wetting tension by virtue of contact with the substrate. Thus, the droplets are deposited

in a more controllable fashion.

In the process described herein, it is possible to provide that the droplet size is such that each active pixel area can be formed by one droplet only, but it will be appreciated that a number of droplets may be required.

The techniques described herein have a significant additional advantage over ink-jet printing in that they do not require the complicated ink-jet head which puts very stringent requirements on the static and dynamic solution properties such as viscosity, drying, wetting angle with the nozzle plate, surface tension, clogging of the ink-jet nozzles, usable solvents for the ink-jet head etc.

For a better understanding of the present invention and to show how the same may be carried into effect reference will now be made by way of example to the accompanying drawings in which:

Figure 1 is a diagram representing the principle of the invention;

Figure 2 is a diagram illustrating deposition using a single pipette;

Figure 3 is a diagram illustrating deposition using a linear array of pipettes;

Figure 4 is a plan view of an array of pipettes;

Figures 5a and 5b are plan and side views respectively of an array for multi-colour deposition; and

Figure 6 is an alternative arrangement for multi-colour deposition;

Figure 7 illustrates stepwise movement of a pipette array;

Figures 8a and 8b illustrates the effect of the "bank";

Figures 9a to 9d illustrate two-layer "banks";

Figure 10 is a plan view of the substrate prior to deposition;

Figure 11 illustrates a number of possible different bank configurations;

Figure 12 illustrates an alternative substrate configuration; and

Figure 13 is a diagram of an OLED.

The basic concept underlying the present invention is to use an array of pipettes to deposit a patterned array of droplets of a solution of a material comprising any solution processible organic semiconductor or conductor. Figure 1 illustrates the basic principle. In Figure 1, reference numeral 2 denotes the substrate for an organic device. As is know in the art, the substrate may be formed of glass or plastic but is normally transparent or substantially transparent. The substrate 2 carries a plurality of first electrode regions 4 which are provided in the form of elongate strips on the substrate 2. The electrode regions 4 can be formed of indium tin oxide (ITO) to form anode regions for individual pixels of the device. The electrode regions 4 can be patterned using any known technique.

The electrode regions 4 are separated by a "bank" of an insulating film 6 which has itself been patterned to provide troughs 8 the bottom of which are in contact with the electrode regions 4 of the device. Patterning of the bank can be by any known technique, such as screen printing, photolithography, micro-contact printing etc. Alternatively, the bank itself can be deposited by using pipettes in line with the selective deposition technique described herein. Thus, the deposition of the bank can be carried out as a pre-step using an array of pipettes, to be followed by a subsequent step of depositing the solution-processible organic semiconductor or conductor.

A plurality of pipettes 10 are illustrated, each aligned with a respective trough 8. The pipettes 10 are connected via a conduit 12 to a reservoir 14 holding the solution to be deposited. Although in Figure 1 a plurality of pipettes 10 are shown each aligned with respective troughs 8 and connected to a common reservoir 14 by a common conduit 12. However, a number of different arrangements are possible as described in the

following. The arrangement of Figure 1 is only used to illustrate the principle of the invention.

The substrate is preferably flat (prior to deposition of the bank regions), and arranged horizontally while the pipettes are arranged substantially vertically. This assists in achieving a uniform film thickness over the areas of spread which are defined between the bank separating portions.

The arrangement of the invention allows dots of solution droplets 16 to be deposited in a controlled fashion with the troughs 8.

Although the word pipette is used throughout to describe the components 10, it will be appreciated that these components take the form of elongate hollow bore tubes which allow a solution to be dropped under the force of gravity from a remote end of the tube connected to the reservoir 14 to the distal end of the tube adjacent the openings of the troughs 8. Other components which could be used to implement the pipettes 10 could be for example micro-pipettes, syringes, protruding nozzles, hollow needles etc. The bores may be conical or cylindrical. In the described arrangement the bore of the pipettes 10 has a cross-sectional area in the range 0.001 mm^2 to 10 mm^2. In the preferred arrangement, the pipettes have a circular bore and the diameter is preferably greater than 50 microns and better still greater than 200 microns. A 50 micron diameter corresponds to the cross-sectional area of roughly 2000 μm^2, and a diameter of 200 microns corresponds to a cross-sectional area of roughly 31,400 μm^2. Pipette arrays useful in the present invention are known in the pharmaceutical, bio and biotechnology fields and thus are not described in detail herein, although modifications may be necessary to allow optimisation of the technique for this purpose. Nevertheless it is noted that they could be made of glass, metal, plastic or ceramic or indeed any suitable material compatible with the solution processible organic material being deposited.

The bank 6 performs an important role in preventing solution droplets 16 from spreading and controlling wetting. Although it is in principle possible to implement the present invention without using a substrate with a predeposited bank, the existence of a bank during deposition enhances the performance of the finished devices. The bank or part of the bank can be removed after deposition so that it is not or only partly present in the finished product.

Selection of the bank's thickness is important to properly contain the deposited droplets 16 within the deposition region without overflowing the bank. A thickness t of 0.5 micron, preferably 5 microns or more and better still 10 microns or more gives acceptable performance. The wetting properties of the bank 6 also need to be taken into account so that at least the top part of a bank is not easily wettable with the solution. Exemplary configurations of the bank are discussed in more detail in the following.

The bank can be deposited and patterned easily at high throughput and cheaply by screen printing. Alternative techniques include standard deposition (spin, blade, miniscus, spray, coating etc) together with photolithographic patterning. Another alternative is micro-contact printing. A further alternative is to use a pipette deposition technique as described herein. Materials for the bank are preferably organic insulating materials for example polyimide, but could also be inorganic.

Figure 2 is a diagrammatic illustration of a system using a single pipette 10. The pipette 10 communicates with the reservoir 14 via the conduit 12. Relative movement is provided between the substrate 2 and the pipette 10 either by allowing for movement of the pipette 10 laterally with respect to the substrate as denoted by arrow A, or by causing movement of the substrate 2 laterally with respect to the pipette 10 as indicated by arrow B or both arrows A and B. To allow for movement of the pipette 10, the conduit 12 can be flexible. Alternatively, the

conduit 12 can be rigid and the entire pipette assembly comprising pipette 10, conduit 12 and reservoir 14 can be made movable. Reference numeral 18 denotes a release mechanism operable under the control of a controller 20. The release mechanism may be operated under pressure, and may be manual or automatic. Although the release mechanism is illustrated at the base of the reservoir, this is purely for diagrammatic purposes. The release mechanism can be located at any suitable position in the pipette assembly.

Figure 3 illustrates deposition using a linear array 22 of pipettes 10. The linear array comprising a plate which is shown in side view in Figure 3 and which has on its underside a plurality of apertures 24 through which the pipettes 10 protrude. In the arrangement of Figure 3, a single line of pipettes 10 is provided in the plate 22. The plate 22 has hollow bores 26 which allow the pipettes 10 to communication with the reservoir 14. The linear array and/or the substrate 2 can move in the x-y plane in either the x or y directions.

Figure 4 illustrates a two-dimensional array 28 of pipettes in a plan view of its underside. Although it cannot be seen in Figure 4, it will be clear that the pipettes 10 protrude from the underside of the array 28 and are regularly arranged in the x and y directions. With a two dimensional array of the type illustrated in Figure 4, the pipettes 10 can be lined up with the required areas of deposition on the substrate 2 and patterning can thus take place in a "one shot" process. In contrast, for the single pipette or linear array of Figures 2 and 3, relative movement is required as already discussed. It is possible to contemplate a wide range of regular or irregular pipette arrangements with or without using step-and-repeat manoeuvres.

Figures 5a and 5b illustrate an array of pipettes 30 for multi-colour deposition. That is, the arrangement of the pipettes is such that they can be aligned respectively with deposition areas which are to be made of different polymers having light-emissive

properties at respectively different wavelengths. The pipettes are labelled 10r, 10g and 10b to denote the fact that they are supplying red, green and blue emissive polymers respectively. They are connected to respective different reservoirs, 14r, 14g and 14b for supplying those respectively different polymers.

Figure 6 illustrates an alternative arrangement in which three linear arrays 32, 34 and 36 are provided for supplying respectively the different light-emissive polymers.

The principle underlying Figures 5a, 5b and 6 can also be extended for depositing other polymers in the same device, for example conducting polymers to constitute charge transport layers.

Figure 7 illustrates how a linear array 22 of the type illustrated in Figure 3 having a smaller number of pipettes than the number of deposited regions required in the finished device can be used by moving the array 22 in a stepwise fashion in the x and y directions. The dotted lines denote future positions of the array 22 as it is subject to multiple passes over the substrate.

In the preceding description it is assumed that there is a single droplet 16 of solution dropped via the pipette 10 onto the deposition region at each position of the pipette 10 or the array 22 respectively. However, it is quite possible to consider multiple passes to supply more than one droplet per position region. It is further possible to use a continuous or semi-continuous stream from the pipette 10 if this is combined with motion of the pipettes 10 relative to the substrate 2. For example, this is particularly useful for making linearly patterned areas with linearly patterned banks. For example, patterning different red, green and blue polymers in stripes is possible for LEPs or patterned fluorescent material. Moreover, it is possible to pattern colour filters for LCD displays in this fashion.

Figures 8a and 8b illustrate the effect of the bank 6. In Figure 8a, a droplet 16 is illustrated over the left-hand-most deposition region before it touches the ITO region 4. To the right of that is shown what happens as the droplet makes contact with the ITO region 4, that is, it is contained by the walls of the bank 6 on either side of the troughs 8.

After a drying step, the device appears as in Figure 8b. That is, the droplet 16 has dried to form layers 38 over the ITO regions 4. These layers 38 are thin film layers of the solution which has been dropped by the pipettes 10. The "flatness" of the thin film layers 38 are controlled by attention to the solution properties, the substrate wetting properties, the bank wetting properties and the flatness of the substrate.

Figures 9a to 9d illustrate a substrate having a two layer bank where the first layer is denoted 6a and the second layer is noted 6b. The first layer 6a can thus be selected of a material having similar wetting properties as indium tin oxide which is used for the electrode regions 4. The second layer 6b can have its edges defining the trough 8 faced away from the edges of the first layer 6a. A plurality of different edge locations are shown in Figures 9a, 9b, 9c and 9d. This allows the height of the second layer 6b to be increased without unduly affecting the wetting properties directly adjacent the indium tin oxide layer, these being controlled by the thinner layer 6a, the ITO and the solution properties. The second layer could be removed so that it is not present in the finished product.

Figure 10 is a plan view which illustrates more clearly how the bank 6 defines apertures or troughs 8 to define active regions p for the device. Reference numeral 4 denotes the strips of ITO as before.

Figure 11 illustrates a number of possible different bank configurations. These shapes could be combined in a two layer structure as shown in Figures 9a to 9d.

Figure 12 illustrates an alternative substrate configuration prior to deposition. In the arrangement of Figure 12, the ITO strips 4 are shown extending laterally, with bank strip 6 extending transversely of the ITO strips 4. This allows the pipette 10 to move along the trough created between the banks 6 to deposit solution in a continuous or semi-continuous stream. After deposition of the solution and drying to produce a film 38, a cathode can be deposited to produce the finished product illustrated in Figure 13. The cathode can for example be of aluminium or a dual layer of aluminium and calcium or any cathode material used for organic LEDs. Thus, in the finished device of Figure 13 the light-emitting device has a structure comprising a substrate 2, a plurality of indium tin oxide strips 4 extending laterally and a plurality of bank bars 6 extending transversely of the indium tin oxide strips 4. Between the strips 6 is formed a thin film of a light-emissive polymer 38 which is the result of a drying step after the solution-processible material has been deposited using the pipette 10. The thin film 38 overlies the indium tin oxide strips 4 and therefore forms active pixels p in the areas of overlap. The cathode 40 overlays the device. When an electric field is applied between the indium tin oxide strips 4 and the cathode 40, charge carriers of opposite types are caused to be injected from the ITO and cathode respectively into the light-emissive layer 38. These charge carriers recombine and then decay radiatively to cause light to be emitted.

While the technique has been described in relation to the manufacture of OLEDs, it will readily be appreciated that other active optic, electronic or opto-electronic devices can be made, for example multi-colour and/or RGB devices, patterned LEPs or fluorescent filters, active or passive matrix, diodes and photo-diodes, triodes, opto-couplers, photovoltaic cells, thin film transistors etc. These devices have in common the fact that they include at least one patterned active organic semiconductor or conductor layer.

The system is preferably used with a controllable drop release

mechanism which is capable of dispersing controllable amounts of the solution onto the substrate. Each pipette can be individually controllable.

While the OLED structure described herein has been described with a substantially transparent substrate 2 with pre-patterned electrode regions of ITO, it will be appreciated that other constructions are possible. By way of example and not as limiting, it is possible to use conductive tin oxide or metal or alloys as the pre-patterned electrodes. Alternatively, the cathode can be deposited at the bottom of the structure, rather than on top as illustrated in Figure 13.

Materials which may be deposited in accordance with the invention include the following:

a) conducting polymers such as polyaniline (PANI) and derivatives, polythiophenes and derivatives, polypyrrole and derivatives, polyethylene dioxythiophene; doped forms of all these and particularly polystyrene sulphonic acid-doped polyethylene dioxythiophene (PEDT/PSS);

b) solution processible molecular compounds including spiro-compounds, such as described for example in EP-A-0676461;

c) solution processible charge transporting and/or luminescent/electro-luminescent polymers, preferably conjugated polymers such as: polyphenylenes and derivatives, polyphenylene vinylenes and derivatives, polyfluorenes and derivatives, tri-aryl containing polymers and derivatives, precursor polymers in various forms, copolymers (including the above-named polymer classes), generally random and block copolymers, polymers with the active (charge transporting and/or luminescent) species attached as side-groups to the main chain, thiophenes and derivatives, etc;

d) other inorganic compounds, e.g. solution-processible organometallic precursor compounds to fabricate insulators or conductors.

In this context, a solution processible material is one which, when dried, generates a final, stable form which is preferably optically/electronically/optoelectronically active. Thus, solutions which, when dried, achieve their final form are included, as are solutions of a precursor polymer which, when dried, convert to the final form of the polymer. One way in which the solution processible material can achieve its final form is by evaporation of solvent to leave a robust solute. This can be accomplished by drying the material or just "leaving it to dry" at RTP (Room Temperature and Pressure). Of course, a drying step on its own may not be sufficient to convert the solution processible material to its final common stable form in which case additional steps may be provided to render the necessary change in chemical composition of the material.

The deposition technique described herein is particularly useful for in-line processing to deposit a number of different materials. That is, a substrate could be moved continuously or step-wise between a number of different bore assemblies for depositing different materials to form different layers.

CLAIMS:

1. A method of selectively depositing a solution-processible organic material by supplying said material through an elongate hollow bore from a remote end in communication with a reservoir of said material to a distal end adjacent a substrate for receiving said material, wherein the supply of said material is controlled such that it leaves the distal end under one or a combination of gravitational force and wetting tension by virtue of contact between said material and the substrate.

2. A method according to claim 1, wherein said at least one hollow bore is in communication with said reservoir via a flexible tube to allow movement of said bore relative to said substrate to permit selective deposition at predetermined regions of the substrate.

3. A method according to claim 1, wherein said elongate hollow bore forms part of a bore assembly which includes said reservoir and which is movable relative to the substrate to allow said selective deposition at predetermined regions of the substrate.

4. A method according to claim 1, wherein the substrate is mounted for movement with respect to said at least one elongate hollow bore to allow said selective deposition at predetermined regions of the substrate.

5. A method according to claim 3, wherein said bore assembly comprises an array in the form of a plate comprising a plurality of apertures each of which is associated with a respective protruding elongate hollow bore, said apertures permitting communication of said bores with said reservoir.

6. A method according to claim 1, which comprises at least three such elongate hollow bores in communication with respective different reservoirs for supplying different material to predetermined regions of the substrate, said different materials

being light-emissive organic materials capable of emitting light at different wavelengths.

7. A method according to any preceding claim, wherein the substrate carries a preformed configuration of separating material for defining predetermined regions where said selective deposition is to take place.

8. A method according to claim 7, wherein an electrode material has been predeposited in said predetermined regions.

9. A method according to any preceding claim, wherein the cross-sectional area of the bore is in the range 0.001 mm^2 to 10 mm^2.

10. A method according to any preceding claim, wherein the distance between the substrate and the distal end of the elongate hollow bore is less than 10 mm.

11. A method according to any preceding claim, wherein the rate of deposition of said material via said elongate hollow bore is less than 3 m/s.

12. A method according to any preceding claim, wherein said predetermined regions have a maximum dimension greater than 50 μm.

13. A method of manufacturing an optic, electronic or optoelectronic device comprising:

(a) forming on a substrate a predetermined configuration of separating material to define predetermined regions for subsequent deposition of a solution-processible material;

(b) depositing a solution-processible material in said predetermined regions by supplying said material from a remote end of an elongate hollow bore in communication with a reservoir of said material to a distal end of said bore adjacent said predetermined regions,

wherein the supply of said material is controlled such that it leaves the distal end under one or a combination of gravitational force and wetting tension by virtue of contact between said material and the substrate; and

(c) performing a drying step.

14. A method according to claim 13 which comprises, prior to step (a), the step of forming on the substrate a plurality of electrode regions, which are exposed at said predetermined regions.

15. A method according to claim 14, wherein said electrode regions are anode regions and the method comprises a further step, after the drying step, of depositing a cathode layer.

16. A method according to claim 13, 14 or 15, wherein the solution-processible material is a light-emissive organic material.

17. A method according to claim 1 or claim 13 wherein said material is brought into contact with the substrate whilst said material is still in contact with the distal end of the bore.

18. A method of producing an active component for an optic, electronic, or optoelectronic device using the method according to claim 1 or claim 13.

Application No: GB 9909418.7 **Examiner:** Richard Kennell
Claims searched: 1-18 **Date of search:** 14 July 1999

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): B1X, B2E (EAA), B2L (LCEC, LCR)

Int Cl (Ed.6): B05B 1/02 1/22; B05C 5/02; B05D 1/26 1/30

Other: Online: WPI, JAPIO, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 2067103 A	(ROBALDO), whole document	1 at least
X	GB 1246749 A	(ASAHI GLASS), see feeding pipe 9 at Figs 3-5, and page 4 lines 116-123	1,10 at least
X	GB 0811838 A	(SANZ), whole document	1 at least
X	EP 0765694 A	(DAI NIPPON PRINTING), whole document	1 at least
X	EP 0127267 A	(DYNATECH LABORATORIES), whole document	1 at least
P,X	WO 98/30904 A	(MERCURY DIAGNOSTICS), 16 July 1998, equivalent GB 2323442 A, see nozzle diameters in claims 6,8	1,9 at least
X	WO 84/02090 A	(WHITEHEAD et al), see tubes 28 at Figs 1-4, tubes 228 at Fig 10 and syringe 350 at Fig 11	1 at least
X	US 5571560 A	(LIN), whole document	1 at least
X	US 5266349 A	(BOK), see orifices 38, 40	1 at least
X	US 5000988 A	(INOUE), whole document	1 at least

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